High speed-low volume automated ICP-QMS method for determination of Mg/Ca in biogenic calcite

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To the Editor of
Journal of Analytical Atomic Spectrometry

Dear Editor,
We have submitted electronically the manuscript entitled: "High speed-low volume automated ICP-QMS method for determination of Mg/Ca in biogenic calcite" by Marco Roman, Patrizia Ferretti, Warren R.L. Cairns, Andrea Spolaor, Clara Turetta and Carlo Barbante, that we wish to publish in *JAAS*.

Please see below also a short description of the novelty of the work.

Novelty of the work

The Mg/Ca molar ratio in foraminiferal calcite accumulated in deep sea sediments is a well established proxy of ancient ocean temperatures. In the shells of foraminifera, Mg can be more than three orders of magnitude less abundant than Ca. Since an empirical exponential equation relates their ratio to the temperature of water surface, the accuracy of calculated temperature depends dramatically on the accuracy and precision of measurements, and the comparability of the results is heavily impacted by standardisation of the analytical methodology.

A number of methods based on ICP-OES and ICP-MS, have been developed and applied for Mg/Ca determination in biogenic calcite, leading to comparably good accuracy and relative precision in the range of 1% or lower. Despite these performance criteria, there are still some margins for improvement of current methods. Since Mg is more than three orders of magnitude less abundant than Ca in foraminifera, measuring both in the same sample dilution or analytical run is difficult without incurring interferences, matrix and memory effects caused by the relatively high Ca concentration. An ideal approach would be the measurement of Mg and Ca in independent sample dilutions under individually optimised instrumental conditions, and possibly recurring to online isotope dilution, but off-line gravimetric double dilution results in doubling the number of samples to be prepared/analysed, and increases contamination risk.

In the present study, we propose a fully automated on-line analytical approach for measuring Mg and Ca in the same sample at distinct dilution levels, under independently optimized instrumental acquisition modes (nogas-H_2 reaction) and with the use of on-line Sc addition as an internal standard, for the quantification of Mg/Ca in biogenic calcite by ICP-CRC-QMS. Matrix effects and instrumental drift are effectively mitigated, as supported by comparison with results from on-line isotope dilution analysis. Memory effects were minimized, and only 20 µg of calcitic material was required for analysis. The method was found to be accurate over the wide range of Mg/Ca values (from 0.8 to 5.7 mmol mol^{-1}) present in the certified reference materials BAM-RS3, ECRM-752-1 and CMSI-1767, with repeatability in the range of 0.3-0.7% and an instrumental LOD of 0.6 nmol mol^{-1}. Test application to five samples of planktonic foraminifera collected from sediments drilled in the North Atlantic Ocean as part of Integrated Ocean Drilling Program, gave results consistent with literature values.

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The improvements provided by this instrumental approach are:

- effective removal of spectral interferences, matrix and memory effects are achieved without any significant increase in preparation or analysis time;
- analytical performances comparable with the state-of-the art, particularly isotope dilution analysis, can be achieved without recurring to gravimetric spiking and at a lower cost;
- the improved LOD allows reducing the required calcitic material to a single shell virtually, making the analysis feasible even when the sample amount is critically low;
- high sample throughput and potential for standardisation are allowed by setup automation;
- in case of inadequate signal intensities, the samples can be re-diluted without complications, whilst maintaining the appropriate level of internal standard;
- the system is easily upgradable to multiple on-line dilutions and multi-elemental ratios without substantial changes in the set-up, and without significant increase of the time/cost for the analysis or the risk of contamination.

We declare that this manuscript has not been previously published and that the data have not been submitted elsewhere for consideration.

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High speed-low volume automated ICP-QMS method for determination of Mg/Ca in biogenic calcite

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Abstract

The Mg/Ca molar ratio in foraminiferal calcite accumulated in marine sea sediments is a well-established proxy of ancient ocean temperatures. Mg is three orders of magnitude less abundant than Ca, and the relationship between their ratio and sea surface temperature is exponential. Consequently, the reliability of the calculated temperature depends dramatically on the accuracy and precision of measurements, and the comparability of the results is heavily impacted by standardisation of the analytical methodology.

Here, we extended the applicability of ICP-QMS for the determination of Mg/Ca in foraminifera, by implementing an automated on-line dual-dilution manifold combined with mixed instrumental acquisition modes (nogas-H_2 reaction), and the use of on-line Sc addition as an internal standard. This allowed the independent acquisition of Mg and Ca at their optimised working concentrations under instrumental conditions that were free of significant spectral interferences. Matrix effects and instrumental drift are effectively mitigated, as supported by comparison with results from on-line isotope dilution analysis. Memory effects were minimized, and only 20 µg of calcitic material was required for analysis. Automation of the setup allowed dual dilution analysis of samples without any significant increase in preparation or analysis time. The system is easily upgradable to multiple on-line dilutions and multi-elemental ratios. The method was found to be accurate over the wide range of Mg/Ca values (from 0.8 to 5.7 mmol mol^{-1}) present in the certified reference materials BAM-RS3, ECRM-752-1 and CMSI-1767, with repeatability in the range of 0.3-0.7% and an instrumental LOD of 0.6 nmol mol^{-1}. Test application to five samples from the Integrated Ocean Drilling Program Site U1313 gave results consistent with literature values.

Keywords

Mg/Ca; biogenic calcite; foraminifera; ocean paleothermometry; ICP-QMS; Integrated Ocean Drilling Program Site U1313.

1. Introduction

The chemical composition of marine biogenic carbonates reflects several chemical and physical properties of the ocean at the time of calcification. Elemental concentrations or ratios in such matrices, collected from marine sea sediment cores, are proxies for temperature and other environmental parameters from which the climate of the past can be reconstructed.[1] The Mg/Ca molar ratio in foraminifera, unicellular marine organisms that secrete a calcium carbonate shell, is a well-established proxy of ancient ocean temperatures[2-6]. An empirical exponential equation relates this variable to the sea water temperature when the organisms were growing.[3,6,7] Consequently, the propagation of uncertainty in the Mg/Ca measurements impacts dramatically on the reliability of the reconstructed temperature. Surrounding sedimentary material and shell surface contaminants are a primary sources of bias, which are typically addressed by adopting well established multi-step cleaning procedures.[8,9].

The quality of the subsequent analysis, typically carried out after final dissolution of the decontaminated shells, is a second key factor. Instruments with ICP sources are commonly used for Mg/Ca measurements, including methods based on quadrupole mass spectrometry (QMS),[10,11] sector field mass spectrometry (SFMS)[12-16] and atomic/optical emission spectroscopy (OES/AES).[17-21] An uncertainty/repeatability of <0.3% and an intermediate repeatability between 1 and 1.5% can be obtained when using both SFMS[14,16] and ICP-OES.[21] A direct comparison between ICP-QMS and ICP-OES has shown that they can also potentially have a similar accuracy and precision.[22] Inter-laboratory comparisons including both techniques have shown that it is possible to obtain an overall reproducibility for Mg/Ca of ~1.5% for planktonic foraminifera[23] and <1.2% for calcite/limestone materials.[24] In recent years, direct analysis of the solid (cleaned) shells has also been explored by laser ablation-ICP-MS with good accuracy and precision ~2-10%,[25-29] but the technique remains under developed particularly due to problems with quantitative calibration.[27]

Despite these performance criteria, there are still some margins for improvement of current methods. Since Mg is more than three orders of magnitude less abundant than Ca in foraminifera, measuring both in the same sample dilution or analytical run is difficult without incurring interferences and matrix effects caused by the relatively high Ca concentration. Modified calibrations in ICP-AES and data correction in ICP-MS are often required to compensate for these factors.[12,17] Spectral interferences can be mostly resolved in ICP-SFMS by operating in medium resolution mode, or mitigated in ICP-QMS by using collision/reaction cell (CRC) or dynamic reaction cell (DRC) technologies. Matrix effects can be compensated for by adopting optimized sample dilution, tuning conditions and calibration strategies, such as external calibration, with and

without internal standard (IS), and isotope dilution analysis (IDA).[13,30,31] Isotope dilution is the most recently used and potentially powerful approach, but is relatively under developed and can be expensive compared to the other strategies. Apart from this, relatively high levels of Ca can result in significant memory effects, which require the use of relatively long washing times between samples.[10] An ideal approach would be the measurement of Mg and Ca in independently optimized sample dilutions under individually optimised instrumental conditions, but off-line double dilution results in doubling the number of samples to be prepared/analysed, and increases contamination risk and error propagation (to avoid this all dilutions should prepared gravimetrically).

In the present study, we propose a fully automated on-line analytical approach for measuring Mg and Ca in the same sample at distinct dilution levels, under independently optimized instrumental conditions with on-line internal standardisation for the quantification of Mg/Ca in biogenic calcite by ICP-CRC-QMS. The method was developed and validated using three calcite/limestone certified materials, spanning the range of Mg/Ca observed in foraminiferal calcite,[24] matrix effects were evaluated by comparison with on-line isotope dilution analysis (ONIDA) results. An explorative application was carried out on five samples of planktonic foraminifera collected from sediments drilled in the North Atlantic Ocean, spanning a time window from ~650 to 700 thousand years (ka) before present, these are replicate analyses of sediments previously analysed by Naafs et al..[32] The advantages of this instrumental approach are the high sample throughput and the potential for standardisation of the analytical methods, , the method also minimises the amount of biogenic calcite required for analysis thanks to the improved LOD.

2. Experimental

2.1. Instrumentation

An Agilent Technologies 7500cx quadrupole ICP-MS (Tokyo, Japan) was used for the determination of Mg and Ca. The instrument was equipped with a PolyPro concentric nebuliser (Elemental Scientific, Omaha, USA), a double-pass Scott spray chamber and an octopole CRC. The cell was used in no gas mode for the acquisition of Mg masses and ^{43}Ca, whereas the reaction mode with H_2 was used for the acquisition of all Ca analytical isotopes. The main operating conditions of the ICP-MS are summarised in Table 1.

The sample introduction system included an ASX-520 autosampler (Cetac Technologies, Omaha, USA) directly connected to the instrument's peristaltic pump. The system was modified for on-line dilution by adding a manifold consisting of a 10-port/2-position switching valve (Valco

Instruments Co. Inc., Houston, USA) controlled by a custom hardware interface and a DOS-based control software, an external 10-channel peristaltic pump (Ismatec, Glattbrugg, CH) and two T-connectors. The configuration and program steps of the manifold are outlined and discussed below. All sample transfer tubing was in PTFE (Grace, Illinois, USA), the peristaltic pump tubing utilised was in Tygon R3607 (Ismatec, Glattbrugg, CH), and all connections were 1/4–28 low pressure Tefzel flangeless fittings (Valco Instruments Co. Inc., Houston, USA).

2.2. Standards and reagents

The standard and spike stock solutions were prepared in LDPE bottles (Nalgene, Rochester, USA). Samples of foraminifera were dissolved in 0.5 mL vials (TreffLab, Degersheim Switzerland) and were subsequently diluted in 15 mL PP centrifuge tubes (Nest, Vetrotecnica, Padova, Italy). The tubes were also used for the dissolution and dilution of the CRMs. To reduce the blanks of these ubiquitous elements, all plastic ware including bottles, tubes and pipette tips - were decontaminated as follows. Bottles and centrifuge tubes were washed sequentially for a week per step in 5%, 1% and 0.1% v/v HNO_3 solutions. After each leaching step, they were rinsed with ultra-pure water and dried under laminar flow hood after the final rinse. The vials 0.5 mL were decontaminated only once in 5% HNO_3 for 24 h. Pipette tips were rinsed twice freshly made 5% v/v HNO_3 solutions and then rinsed three times in ultra-pure water before use. All decontamination steps were carried out in a class 10000 clean room environment under a class 1000 HEPA laminar flow bench.

Ultrapure grade HNO_3 and HCl (Romil, Cambridge, UK) were used throughout the study. All dilutions of standards and samples were prepared in 2% v/v ultrapure HNO_3. High-purity deionised water (18 MΩ·cm) was produced using a Purelab Ultra unit (Elga, High Wycombe, UK), this was used to produce all analytical solutions, the washing solutions and prepare sample dilutions. The cleaning protocol for foraminifera required methanol, hydrogen peroxide, and ammonium hydroxide solution (Romil, Cambridge, UK), hydrazine hydrate solution, citric acid monohydrate, and sodium hydroxide monohydrate were all purchased from Sigma-Aldrich (Milan, Italy).

Quantification by ONIDA was performed using isotopically enriched ^{26}Mg and ^{44}Ca purchased from Spectra2000 S.r.l. (Rome, Italy). The ^{26}MgO powder was dissolved in a solution of 5% v/v ultrapure HCl whereas $^{44}CaCO_3$ powder was dissolved in 5% v/v ultrapure HNO_3. The measured enrichment factor of the spike solutions, as reported in Table 2, was >99%. Stock and intermediate calibrations solutions of natural abundance Mg, Ca, and Sc as the IS were prepared from ICP-MS grade 1000 ng g^{-1} standard solutions (Ultra Scientific, Bologna, Italy).

2.3. Samples

Three CRMs were used throughout the study to validate the method for the determination of Mg/Ca, namely the limestone ECRM-752-1 (LCG, Teddington, UK) and CMSI-1767 (Metallurgical Standardisation Research Institute, China), and calcium carbonate BAM-RS3 (Bundesanstalt für Materialforschung und prüfung, Berlin, Germany). The materials were not originally certified for their Mg/Ca ratio, but have been widely used for such determinations in the literature, including within a dedicated interlaboratory comparison.[24] Theoretical values of Mg/Ca and the respective uncertainties are reported in Table 3, these were calculated from the certified values for Mg or MgO, and $CaCO_3$ or CaO. Six replicates of each material were prepared independently by weighting 5-10 mg of powder. The CRMs were dissolved in 10 mL of 0.075 M HNO_3 solution and were then diluted with 2% v/v HNO_3 before analysis.

The foraminifera used in the applicative test were obtained from sediments recovered from the Integrated Ocean Drilling Program (IODP) Expedition 306, Site U1313, drilled in the North Atlantic Ocean on the upper middle western flank of the Mid-Atlantic Ridge, at 41°00′N 32°58′W in a water depth of 3426 m.[33] The sediment was sampled in 1-cm thick segments, averaging ~15 g of dry weight. Bulk sample processing followed standard procedures as can be found elsewhere.[34] The planktonic foraminifera *Globigerina bulloides* were hand-picked from the 315-355 µm coarse fraction of sediment samples; the size of all specimens was constrained in order to limit ontogenetic effects and at least 25 specimens were selected and pooled for each analysis. This species, which is abundant and well preserved at Site U1313, is a mixed-layer dweller that can be found in the North Atlantic throughout the upper 60 m of the water column, and is therefore a recorder of surface water conditions.[35] Five samples were collected, uniformly spanning the interval between the interglacial period Marine Isotope Stage (MIS) 17 and the glacial period MIS 16 (650-700 ka)‡. After being crushed between clean glass plates, the samples were examined under a high magnification stereo-microscope for any remaining coarse grained-silicates and any particles that were not apparently carbonate, these were removed using a fine brush. All samples were then transferred into 0.5 mL vials and treated with a standard cleaning protocol before dissolution.[32] In short, the cleaning process involved the following steps: i) removal of clay and fine-grained carbonates from the crushed foraminiferal shells by multiple rinses with ultra-pure water and methanol, aided by brief intervals of ultrasonication; ii) reductive removal of secondary Mn- and Fe-oxide coatings by using a mixture of hydrazine hydroxide, citric acid and ammonia hydroxide in a boiling water bath assisted by ultrasonication; iii) removal of organic matter by reaction with an oxidising solution (H_2O_2 1% v/v in 0.1 M NaOH solution) in a boiling water bath with brief intervals of

ultrasonication; iv) removal of coarse grained-silicates and any particles that were not apparently carbonate using a fine brush under the microscope; v) removal of any adsorbed contaminants - particularly secondary $MnCO_3$ overgrowths - from the test fragments by reaction with a weak acid solution (0.001 M HNO_3) followed by rinsing with ultra-pure water to prevent extensive dissolution of the sample. The samples were finally dissolved in 400 µL of a 2% v/v HNO_3 solution; ultrasonicated for a few minutes to promote dissolution; and any possible insoluble impurities were removed by centrifugation at 6000 rpm for 5 min. The supernatant (375 µL) was transferred into clean tubes and diluted 1:100 in 2% v/v HNO_3.

Sample preparation was always carried out in a clean room environment; all samples of CRMs and foraminifera were dissolved and analysed on the same day.

2.4. Dual sample dilution-internal standardisation for the quantification of Mg/Ca

The developed analytical strategy consists of the independent acquisition of Mg and Ca in distinct dilutions of the same sample. The first dilution is to obtain a working concentration of approximately 10 ng g^{-1} of Mg (calculated from the typical sample weight and the average value of the expected range of molar ratios for Mg/Ca of 2 mmol mol^{-1}) with acquisition using nogas conditions. Ca is determined after further dilution of the first solution to approach a working concentration of 200 ng g^{-1}, with acquisition in H_2 reaction mode. The IS Sc is added on-line for the quantification of both elements. The final molar ratio is calculated from the two concentrations using the formula:

$$R = DF \cdot \frac{Aw_{Ca}}{Aw_{Mg}} \cdot \frac{k_{Ca}}{k_{Mg}} \cdot \left(\frac{^{24}Mg}{Sc_{nogas}} / \frac{^{40}Ca}{Sc_{H_2}} \right) \quad \text{eq.1}$$

where k_{Mg} and k_{Ca} are the slopes of independent calibration curves for each element, DF is the dilution factor between the first and the second dilution, and $Aw_{Ca,Mg}$ are the atomic weights. The calibration was constructed with 5 standard solutions containing both Mg and Ca at linearly increasing concentrations that also linearly increased the molar ratios as well.

In our method, a solution containing the IS was mixed on-line with the sample using a T-connector. A spike solution-to-sample flow ratio of ~1:10 was used after choosing pump tubes with different internal diameters, the actual flow ratio was measured gravimetrically on the day. A variety of tubes (0.18 to 1.85 mm id with two-stops for the external pump; 0.25 to 1.1 mm id three-stops for the ICP-MS pump) were tested by determining the delivered flow rate as a function of the pump speed. All tubes guaranteed high linearity (R^2 >0.999), enabling an accurate optimisation of the desired flows by selecting the most appropriate combination of tube diameter and pump speed.

The preservation of linearity was crucial when the pump speed was changed during acquisition (see below). The stability of the spike-to-sample flow rate ratio was demonstrated both during acquisition (RSD of the Sc signal <1%) and between runs (determined gravimetrically for each sample after analysis). This allowed us to cancel out the term relative to the spike flow in eq. 1; however, its uncertainty must still be taken into account in the final uncertainty budget.

Matrix effects on accuracy were determined by comparison with ONIDA results. In ONIDA, isotopically enriched Mg and Ca standard solutions take the place of the elemental IS solution. Although this strategy doesn't exploit the global improvement in accuracy allowed by classical IDA, in which calibrated isotopic spikes are gravimetrically mixed and equilibrated in the sample as early as possible during preparation, to compensate for any possible bias induced by all following analytical steps. On-line isotopic spiking does allow a virtually perfect compensation for instrumental matrix effects and drift, an advantage that makes this approach particularly useful for the quantification of transient signals with a varying matrix composition (such as in hyphenated techniques). In this work, ^{24}Mg and ^{40}Ca were used as the reference isotopes, and ^{26}Mg and ^{44}Ca were adopted as the isotopic spikes. The IDA formula is then used to obtain the molar ratio:

$$R = DF \cdot \frac{C_{sp}^{Mg} \cdot A_{sp}^{26} \cdot \left(R_m^{24/26} - R_{sp}^{24/26}\right) \cdot Aw_{sp}^{Ca} \cdot A_s^{40} \cdot \left(1 - R_m^{40/44} \cdot R_s^{44/40}\right)}{C_{sp}^{Ca} \cdot A_{sp}^{44} \cdot \left(R_m^{40/44} - R_{sp}^{40/44}\right) \cdot Aw_{sp}^{Mg} \cdot A_s^{24} \cdot \left(1 - R_m^{24/26} \cdot R_s^{26/24}\right)} \qquad \text{eq.2}$$

where DF is the dilution factor between the first and the second dilutions, $C_{sp}^{Mg,Ca}$ are the concentrations of Mg and Ca in the isotopic spike, $Aw_{sp}^{Mg,Ca}$ are the atomic weights of Mg and Ca in the spike, $A_{s,sp}^{X}$ are the isotopic abundances of the isotope X in the sample and in the spike, $R_{m,s,sp}^{X/Y}$ are the ratios of the isotopes X and Y in the mixture, the sample and the spike. Mg and Ca masses are acquired independently in separately diluted samples under the instrumental conditions as reported above for the use of elemental IS.

2.5. Automated on-line dilution/spiking manifold

An automated manifold was designed for the sequential analysis of two dilution levels from the same sample. The set-up employs a 10-port/2-position switching valve and an external peristaltic pump, as shown schematically in Fig. 1.

The peristaltic pump of the ICP-MS delivers the sample, while the external pump delivers the diluent HNO_3 solution (2% v/v) and the IS (or isotopic) spike. A starting dilution of the sample is prepared manually with a concentration of the order of 10 µg g^{-1} of Ca, which corresponds to ~10 ng g^{-1} of Mg if the Mg/Ca ratio is 2 mmol mol^{-1} (the mean expected ratio in our real samples). The

manifold works by following an automated time programme coordinated with the start of the ICP-MS acquisition method, as shown in Fig. 1. The analysis of each sample starts with the 10-port valve in position B: the sample is taken up using the large bore tubing and a fast ICP peristaltic pump rotation (0.3 rpm). Immediately before the sample fluid reaches the valve, the latter switches to position A so that sample uptake is governed by the narrow bore tubing, and the flow is diluted on-line with the HNO_3 2% diluent solution. When the sample reaches the nebuliser, the speed of the ICP peristaltic pump is reduced to 0.04 rpm to obtain a final 50-fold dilution, the signal stabilises for a fixed period and the acquisition of Ca under the H_2 reaction mode is performed. The valve then switches to position B, and the sample uptake rate is set by the large bore tubing at a higher flow rate for the undiluted acquisition of the Mg signal. The Final flow rates of approximately 0.3 and 0.7 mL min^{-1} for the two acquisition steps are mixed on-line with an additional constant flow of IS, and are delivered together to the ICP source.

The dilution manifold is used to analyse each sample in dual dilution mode during the same analytical run. For each sample, Mg is measured in the undiluted flow directly after Ca, this means that possible memory effects can be important. However, the manifold is designed so that when one line is being used, the other is being washed with the HNO_3 dilution solution, and vice versa; the spray chamber and other quartz parts of the ICP are washed during the uptake steps. Consequently, the post-analysis rinse steps are limited to cleaning the autosampler lines so the time needed is significantly reduced.

3. Results and discussion

3.1. Optimisation of experimental ICP-QMS parameters

The operating conditions of the sample introduction system and mass spectrometer (see Table 1) were optimised to reach the best signal-to-noise ratio, whilst suppressing spectral interferences, and working in pulse counting mode within as wide a concentration range as possible. As previously reported for the same ICP-MS instrument,[36] both Mg and Ca have the highest signal intensities under hot plasma conditions (we selected 1500 W of RF power).

The most abundant isotope of Mg, *m/z* 24, can be significantly interfered by $^{48}Ca^{2+}$ in calcite samples. Considering an average Mg/Ca of 2 mmol mol^{-1} and a doubly charged ion ratio of 3% based on the $^{140}Ce/^{140}Ce^{+}$, the potential interference can be estimated as 1-5% of the ^{24}Mg signal; this means that reducing the formation of doubly charged ions is key. The high RF power used, in combination with an elevated sampling depth (8 mm) and a reduced carrier gas flow rate (<1.1 mL

min^{-1}), allowed us to maintain oxide and double charged species ratios below ~1% of the parent ion abundance. The resulting apparent concentration of ^{24}Mg was <5 pg per µg of Ca, making the isotope suitable for any realistic interfering concentration of Ca. Overall, using the selected instrumental conditions, the whole isotopic pattern of Mg can be acquired free of significant spectral interferences.

In general, elevated working concentrations of Ca are considered to be a guarantee of high signal-to-noise ratios,[10,12] and constrain the foraminiferal intraspecific variability. However, at such levels, memory effects can force the adoption of longer washing times between samples,[10] meaning ICP-OES has comparable performance, as it is more robust and cheaper than ICP-MS.[22] The independent acquisition of Ca at lower concentrations than those required for Mg monitoring, was simplified by automated on-line dilution, and improved the potential of ICP-QMS by allowing dedicated optimisation of instrumental conditions to minimise matrix and memory effects. This also overcome the need to monitor only the low-abundance isotopes of Ca (typically ^{43}Ca, still is potentially affected by the $^{27}Al^{16}O^{+}$ isobaric interference). We opted for a working concentration of 200 ng g^{-1} of Ca, combined with the use of H_2 reaction mode, which effectively mitigates the major spectral interferences on both ^{40}Ca and ^{44}Ca (respectively $^{40}Ar^{+}$, and $^{12}C^{32}S^{+}$, $^{28}Si^{16}O^{+}$) down to a background equivalent concentration (BEC) of <1% for Ca (see Fig. 2). Notably, using ^{40}Ca as the reference isotope makes ^{44}Ca usable as the enriched spike in ONIDA, with the advantage that is 6 times cheaper than ^{43}Ca (from a quote by Isotope Cambridge Laboratories), previously used by Fernandez et al..[31] No significant interference of $^{44}CaH^{+}$ on the signal of the IS Sc at *m/z* 45 was observed at concentrations of Ca <20 µg g^{-1}, even when using H_2 as a reaction gas. Overall, the selected instrumental conditions allow the acquisition of the whole isotopic pattern of Ca free of significant spectral interferences.

The integration time was optimised to maintain the RSD of all intensity ratios <1%. We observed no significant advantage in terms of precision for signal ratios when integration times were reduced and the number of replicate acquisitions increased, as done by other authors.[31]

As mentioned above, the working concentrations of Mg and Ca, and the operating parameters were optimised to ensure, where possible, that all signals were acquired in pulse counting mode. However, when foraminifera samples are to be analysed, they must undergo a complex cleaning procedure that entails a non-quantifiable reduction in their sample weight, which in turns shifts the actual concentration of the elements with respect to their theoretical levels. Thus, if a pre-analysis of the samples is not possible, an estimation and frequent (intra-run) update of the pulse counting-to-analog conversion factor is strongly recommended to ensure alignment of the two detector modes.

Prior to the application of ONIDA, the instrumental mass bias was determined, isotopic spike materials were characterized, and the optimum sample-to-spike mixing ratio was estimated as reported elsewhere.[31] The mother solutions containing enriched ^{26}Mg and ^{44}Ca were preliminarily characterised for their isotopic abundances, and their concentrations determined based on the principle of reverse IDA. A concentration of 200 ng g^{-1} for ^{26}Mg and 2.6 µg g^{-1} for ^{44}Ca as a working spike solution was selected to obtain the optimum isotopic ratio in the mixture according to error propagation theory,[37] assuming a Mg/Ca molar ratio in the sample close to 2.5 mmol mol^{-1}. This approach for ONIDA differs from IDA proposed by Fernandez et al.,[31] (with off-line gravimetric spiking) where Ca was monitored at 100-200 times higher concentrations, and *m/z* 48 and 43 were used as the reference and spike isotopes (monitored in nogas conditions).

3.2. Analytical figures of merit

Many authors observed matrix effects resulting in a suppression of the Mg signal with increasing Ca concentrations within the range 4-1000 µg g^{-1},[12,13,22,38] this suppression represents 5-10% of the Mg/Ca value when Ca is in the range 60-320 µg g^{-1} when using ICP-SFMS.[16] Other authors did not see these effects when Ca was maintained below 40-200 µg g^{-1}.[10,31]

In this paper, calibration standards were prepared with a mixture of variable concentrations of Mg (0.6 to 48.5 ng g^{-1}) and Ca (2 to 20 µg g^{-1}), so that their resulting molar ratios varied from 0.5 to 4 mmol mol^{-1}. A linear suppression of the Mg signal would have resulted in a nonlinear Mg calibration, whereas a nonlinear suppression would have resulted in a nonlinear Mg/Ca ratio calibration. However, as shown in Fig. 3, such effects were not observed as linearity was maintained in all cases over replicate calibrations. At the working concentration of 10 µg g^{-1}, close to the lower limits of the range explored by other authors, matrix effects appear to be negligible with our instrumental set-up (with a guard electrode) and operating conditions. Since no correction for matrix effects is required, its contribution to the final combined uncertainty can be removed.

The overall accuracy for the analysis of Mg/Ca molar ratio in the three CRMs is comparable to the literature and theoretical values, as shown in Table 3. The Mg/Ca ratio in CMS-1767 was slightly lower (by ~6%) compared to the literature values, an effect which was probably due to the switch to analogue mode for the monitoring of ^{24}Mg at higher concentrations. The imperfect alignment of the pulse/analogue acquisition modes constitutes a potential problem, as mentioned by other authors.[12,13] Maintaining the acquisition in pulse mode is preferable because lower concentration levels can be used and counting statistics improve. Although Mg/Ca molar ratios can

cover a wide range in biogenic carbonates, the Mg/Ca in calcitic foraminiferal shells is normally reconstructed by analysing monospecific samples, meaning that the range is more limited. This implies that dilutions can be driven by theoretical information to avoid mixed mode acquisitions. Accuracy was not statistically different between IS and ONIDA, confirming the absence of matrix effects.

The repeatability (RSD) for CRMs is also globally comparable between the proposed approach and the literature, as shown in Table 4. The repeatability was also calculated in the combined form (CRSD), taking into account the uncertainty associated with the calibration, and was divided in its components between and within replicates. Since the application of methods to real samples is usually limited to single replicates, the RSD between replicates this becomes an index of the expected accuracy of a single measurement. The within replicates RSD is also important as it estimates the average precision of the single measurements. A RSD between replicates ≤0.7% was globally obtained, and was particularly low (0.3%) for BAM-RS3, which was the more critical material due to the low concentration of Mg.

Our approach based on dual dilution was conceived to measure Ca at much lower concentrations compared to most alternative methods (Table 5), allowing us to reduce possible matrix and memory effects. The LODs of the Mg/Ca ratio, forced by those of Mg, are also considerably reduced. Combined with a mL-level sample introduction system, the method can be applied to sample weights in the lowest available range. If coupled to a micro-volume autosampler, the method could result in a reduction of sample weight to 2 µg, whilst maintaining the same working concentrations. The actual relevance of sample weight and LOD reduction should be assessed as they depend on the characteristics of the samples and the goals of the specific applicative study. Some works on method development propose a reduction of sample weight to the level of a single foraminifera.[39] This strategy allows a reduction in sample size, thereby shortening the preparation steps, particularly the picking of selected specimens for analysis. However, a procedure that uses only a single shell does not constrain the intraspecific variability and can be severely affected by potential noise due to post-depositional processes, such as bioturbation and reworking. This means that one or a few shells may be not sufficient to obtain reliable data. Similarly, the instrumental set-up should be designed depending on the expected range of Mg/Ca ratios, which can be restricted by selecting certain species and geographical provenances, so that an extremely low LOD could become irrelevant in practice.

3.3. Determination of Mg/Ca molar ratios in *G. bulloides*

The methodology was applied to the determination of the Mg/Ca molar ratios in geological samples of foraminiferal calcite. Five representative samples were selected from the sedimentary succession already analysed by Naafs et al.,[32] and were prepared following the same standard cleaning protocol, aimed at removing contaminants including clays, Mn/Fe oxides, manganese carbonate overgrowths, and organic matter trapped within the chambers or coated on the shell surfaces during diagenesis. The samples were selected from the interglacial period MIS 17, the MIS 16 glacial inception, and the full glacial conditions during MIS 16. The measured Mg/Ca ratios are reported in Table 6, while Fig. 4 represents the sea surface temperature correspondingly reconstructed using the calibration equation by Elderfield and Ganssen.[3] The average combined uncertainty of all single measurements was 1.0%, with contribution calibration curves accounting for 0.3% and 0.5% of this uncertainty for ^{24}Mg/IS and ^{40}Ca/IS, respectively. The obtained Mg/Ca ratios agree with those reported by Naafs et al.[32] within 15%, resulting in consistent temperature estimates (see Fig. 4).

4. Conclusion

The reconstruction of ocean surface paleotemperature is crucial for the comprehension of the mechanisms underlying climate variability. The Mg/Ca molar ratio in foraminiferal and other biogenic carbonates is a powerful proxy for seawater temperature. Its pairing with calcite $\delta^{18}O$ permits us to remove the temperature component from the isotopic signal, and to calculate the $\delta^{18}O$ of seawater, which contains a global glacioeustatic signal, another key variable for paleoclimate studies.[3] Improving method accuracy, reproducibility, robustness and standardisation for multi-elemental ratio determinations in marine biogenic carbonates are fundamental to strengthen their reliability as paleothermometers.[24]

In this study, we have developed an improved approach for the use of ICP-QMS determination of Mg/Ca by combining an automated on-line dual-dilution manifold with interference suppression by CRC (H_2), and the use of Sc as the internal standard. This approach allows independent acquisition of Mg and Ca at individually optimised working concentrations and instrumental conditions, free of significant spectral interferences for the whole isotopic pattern. With low levels of Ca, and on-line IS spiking, matrix effects and instrumental drift are effectively mitigated, and are comparable to the application of ONIDA. The minimum absolute amount of calcitic material required for the analysis is 20 µg, with potential further reduction to <10 µg (virtually equivalent to a single shell) if using a micro-volume autosampler. The instrumental method was accurate over a wide range of Mg/Ca values (from 0.8 to 5.7 mmol mol^{-1}) present in the BAM-RS3, ECRM-752-1

and CMSI-1767 CRMs, with repeatability in the range of 0.3-0.7% and an instrumental LOD of 0.6 nmol mol^{-1}.

Additional advantages are achieved by analysis automation: i) two dilutions of each sample can be analysed without significantly increasing the preparation or analysis time; ii) memory effects and wash time are minimized; iii) in case of inadequate signal intensities, the samples can be re-diluted without complications, whilst maintaining the appropriate level of internal standard. iv) extending the approach to multiple dilutions and other elements of interest (each acquired under specific instrumental conditions) is easily possible; v) direct coupling to automated sample cleaning setups[21] is technically possible.

Acknowledgements

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Notes and references

‡ The samples named A-E correspond to the following IODP identification code, respectively: A) 306-1313-A-4H-3W,72-73; B) 306-1313-A-4H-4W,18-19; C) 306-1313-A-4H-4W,97-98; D) 306-1313-A-4H-4W,137-138; E) 306-1313-A-4H-5W,34-35.

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Figure captions

Fig. 1. Above: scheme of the sample introduction set-up for the automatic on-line implementation of a dual dilution strategy. The two positions A and B of the 10-ports switching valve are represented. Tygon tubes were: two stops 1.65 and 0.25 mm i.d. for HNO_3 and IS (respectively) for delivery by the external pump; three stops 1.02 and 0.25 mm i.d. for concentrated and diluted (respectively) sample delivery by the ICP pump. The bold lines mark the flow delivered to the ICP-MS. Below: scheme of the synchronised cyclic ICP-MS/valve time programme.

Fig. 2. Effect of H_2 flow rate on the sensitivity and background equivalent concentration (BEC) for *m/z* 40 (a) and 44 (b) measured in a standard solution of Ca 100 ng g^{-1} and a blank solution.

Fig. 3. Examples of independent Mg and Ca calibration curves (a, b), and the resulting Mg/Ca ratio calibration curve (c), obtained using the on-line dilution manifold. The concentration of Ca reported in the x-axis is that in the solution, without considering the 50-fold dilution performed on-line.

Fig. 4. Shallow subsurface temperature estimates at Site U1313, based on Mg/Ca from the mixed-layer-dwelling planktonic foraminifera *G. bulloides*. The black line and the grey area represent the values reported by Naafs et al.[32] and the corresponding confidence band (± 1·combined SD).

Table 1. ICP-CRC-QMS main operating conditions.

RF power	1500 W	
Plasma gas flow rate	15 L min^{-1}	
Ions lens setting	Optimised daily for best sensitivity of 10 ng g^{-1} Li, Co, Y and Tl, in a 1% (v/v) HNO_3 solution	
Sampling depth	8 mm	
Spray chamber temperature	2°C	
Points per peak	3	
Acquisition time per mass	1 s	
Replicates	5	
	Mg (Ca)	Ca
Carrier gas flow rate	1.08 mL min^{-1}	1.18 mL min^{-1}
Collision/reaction cell	nogas	H_2 5.7 mL min^{-1}
Monitored *m/z*	24(26),45	40(44),45

Table 2. Atomic weight (± SD) and isotopic abundances (atom % ± SD) of all isotopes in natural and spiked Mg (10 ng g^{-1}) and Ca (200 ng g^{-1}) standard solutions. *Compared to the average of the standard range.

	Standard (IUPAC)[40,41]	Measured (bias-corrected)	
	Natural	Natural (accuracy %)	Isotopic spike
^{24}Mg	[78.8-79.95]	78.982 ± 0.142 (100)*	0.406 ± 0.127
^{25}Mg	[9.988-10.034]	9.992 ± 0.018 (100)*	0.143 ± 0.013
^{26}Mg	[10.96-11.09]	11.025 ± 0.012 (100)*	99.451 ± 0.116
Atomic weight	[24.304-24.307]	24.305 ± 0.035 (100)*	25.973 ± 0.043
^{40}Ca	96.941(156)	96.893 ± 0.943 (100)	0.857 ± 0.450
^{42}Ca	0.647(23)	0.658 ± 0.005 (102)	0.052 ± 0.010
^{43}Ca	0.135(10)	0.138 ± 0.002 (102)	0.025 ± 0.003
^{44}Ca	2.086(110)	2.120 ± 0.012 (102)	99.034 ± 0.430
^{46}Ca	0.004(3)	0.004 ± 0.007 (100)	0.007 ± 0.008
^{48}Ca	0.187(21)	0.188 ± 0.003 (101)	0.026 ± 0.003
Atomic weight	40.078(4)	40.080 ± 0.377 (100)	43.921 ± 0.261

Table 3. Mg/Ca molar ratio (mmol mol^{-1}, average ± SD, n=6) determined in the three certified reference materials in comparison with the literature values.

		BAM-RS3	ECRM-752-1	CMS-1767
Theoretical value		0.76 ± 0.02*	3.77 ± 0.25**	6.05 ± 0.50**
Freitas et al.[20]	ICP-AES	0.78 ± 0.12	3.82 ± 0.07	5.76 ± 0.07
Greaves et al.[24#]	ICP-MS/OES	0.775 ± 0.043	3.824 ± 0.095	5.733 ± 0.142
Fernandez et al.[31]	ICP-QMS/SFMS, IDA	0.80 ± 0.01	3.86 ± 0.02	5.67 ± 0.05
This study	ICP-QMS, IS	0.774 ± 0.002	3.901 ± 0.025	5.407 ± 0.037
	ICP-QMS, ONIDA	0.775 ± 0.008	3.883 ± 0.046	5.359 ± 0.036

*calculated from data provided by the certificate of analysis: certified mass content of Mg, sample purity as $CaCO_3$, and respective uncertainties.

**calculated from data provided by the certificate of analysis: certified mass content of MgO, CaO, and respective uncertainties.

[#]Average repeatability from all laboratories (no outliers removed); uncentrifuged samples.

Table 4. Repeatability of Mg/Ca molar ratio in the three reference materials calculated as RSD% and combined RSD% between/within replicates (n=6).

		Between replicates						Within replicate		
		RSD%			CRSD%			CRSD%		
		BAM RS3	ERCM 752-1	CMSI 1767	BAM RS3	ERCM 752-1	CMSI 1767	BAM RS3	ERCM 752-1	CMSI 1767
Freitas et al.[20]	ICP-AES	15.4	1.8	1.2						
Greaves et al.[24]*	ICP-MS/OES	1.6	0.7	0.8						
Fernandez et al.[31]	ICP-QMS/SFMS, IDA	1.3	0.4	0.4						
This study	ICP-QMS, IS	0.3	0.6	0.7	0.7	1.4	1.5	1.7	2.2	2.0
	ICP-QMS, ONIDA	1.0	1.2	0.7	2.2	2.6	1.5	3.6	1.3	1.4

*Average repeatability from all laboratories (no outliers removed); uncentrifuged samples.

Table 5. Working conditions and LOD of the methods compared with selected literature.

		[Ca] mM	Vol. mL	Sample wt. µg	Mg/Ca LOD* nmol mol^{-1}
Sun et al.[11]	ICP-QMS	12.5	10	500	n.a.
Wara et al.[18]	ICP-OES	≤ 2.4	0.5	100-1000	58
Yu et al.[610]	ICP-QMS	2.5	0.25	60	15
Marchitto et al.[13]	ICP-SFMS	≤ 2	0.5	10	n.a.
Shen et al.[39]	ICP-QMS	0.15	0.25	3.5	n.a.
Fernandez et al.[31]	ICP-QMS/SFMS, IDA	≤ 1	0.2	10	n.a.
This study	ICP-QMS, IS	0.25[a]/0.005[b]	2.5	20	0.6
	ICP-QMS, ONIDA	0.25[a]/0.005[b]	2.5	20	1.6

*The limiting factor for the ratio is the concentration of Mg; [a]for determination of Mg; [b]for determination of Ca.

Table 6. Measured Mg/Ca (mmol mol^{-1}, average ± combined SD) in test samples from IODP Exp. 306, Site U1313, compared to previous data.

Sample	Naafs et al.[32]	This study
A	2.872 ± 0.107	2.838 ± 0.040
B	2.516 ± 0.108	2.707 ± 0.029
C	1.958 ± 0.155	1.974 ± 0.020
D	1.553 ± 0.108	1.779 ± 0.013
E	1.438 ± 0.112	1.494 ± 0.014

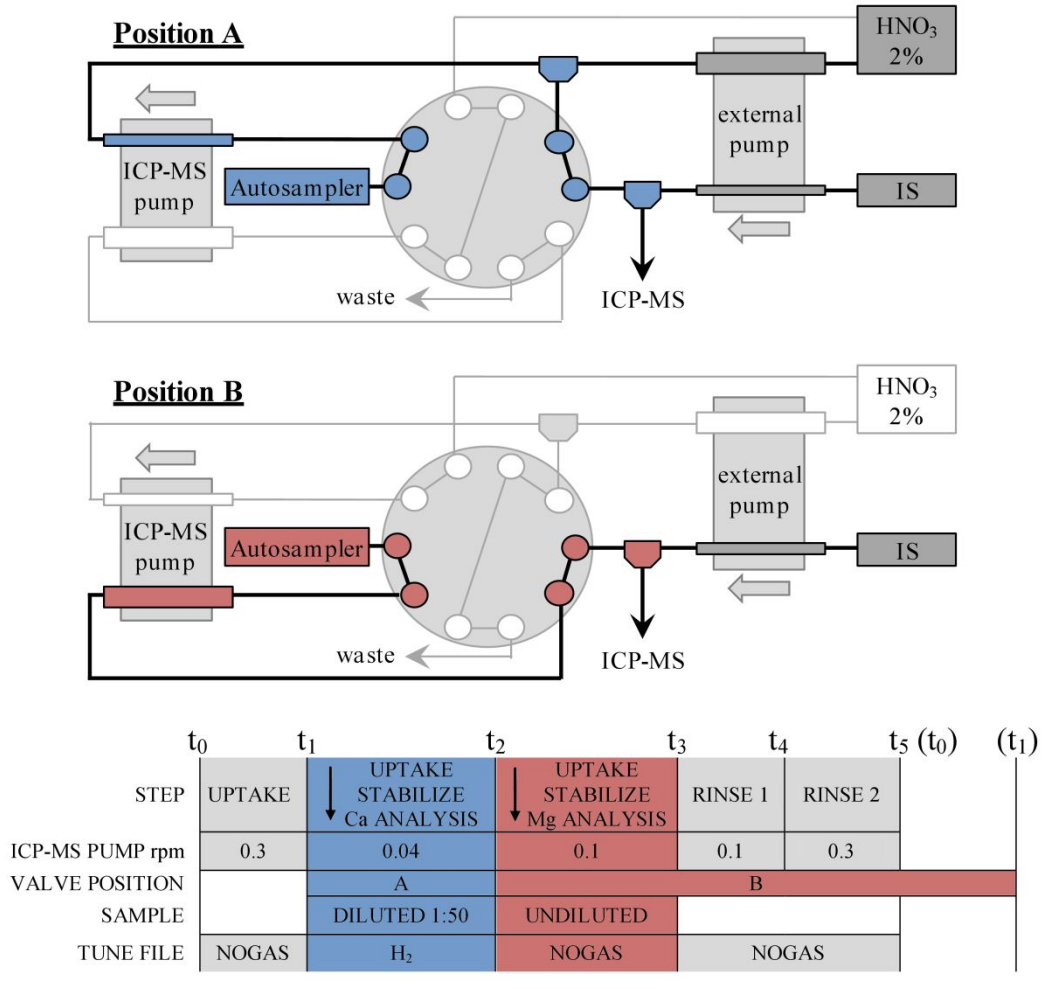

Position A
HNO3 2%
external pump
ICP-MS pump
Autosampler
IS
waste
ICP-MS
Position B
HNO3 2%
external pump
ICP-MS pump
Autosampler
IS
waste
ICP-MS
t0 t1 t2 t3 t4 t5 (t0) (t1)
STEP
UPTAKE
UPTAKE STABILIZE Ca ANALYSIS
UPTAKE STABILIZE Mg ANALYSIS
RINSE 1
RINSE 2
ICP-MS PUMP rpm
0.3
0.04
0.1
0.1
0.3
VALVE POSITION
A
B
SAMPLE
DILUTED 1:50
UNDILUTED
TUNE FILE
NOGAS
H2
NOGAS
NOGAS

Fig. 1

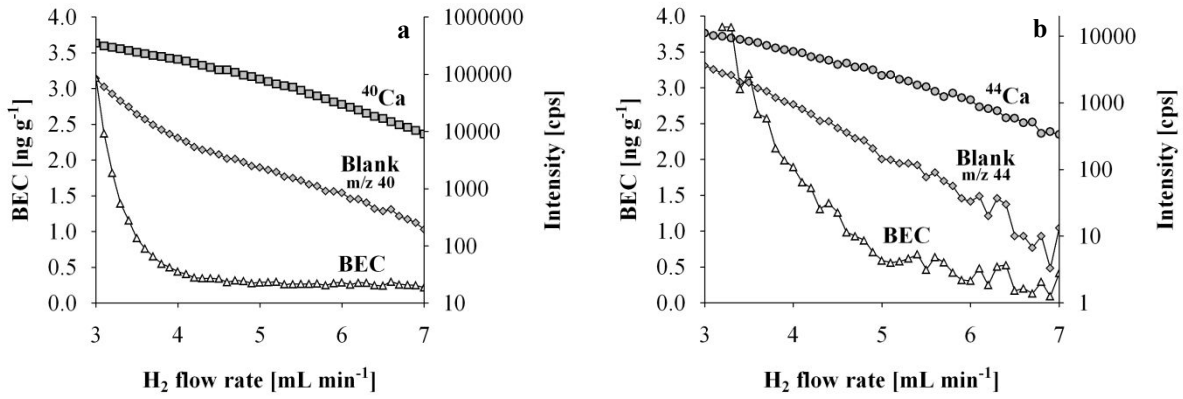

a
b
BEC [ng g-1]
Intensity [cps]
40Ca
44Ca
Blank
m/z 40
m/z 44
BEC
H2 flow rate [mL min-1]

Fig. 2

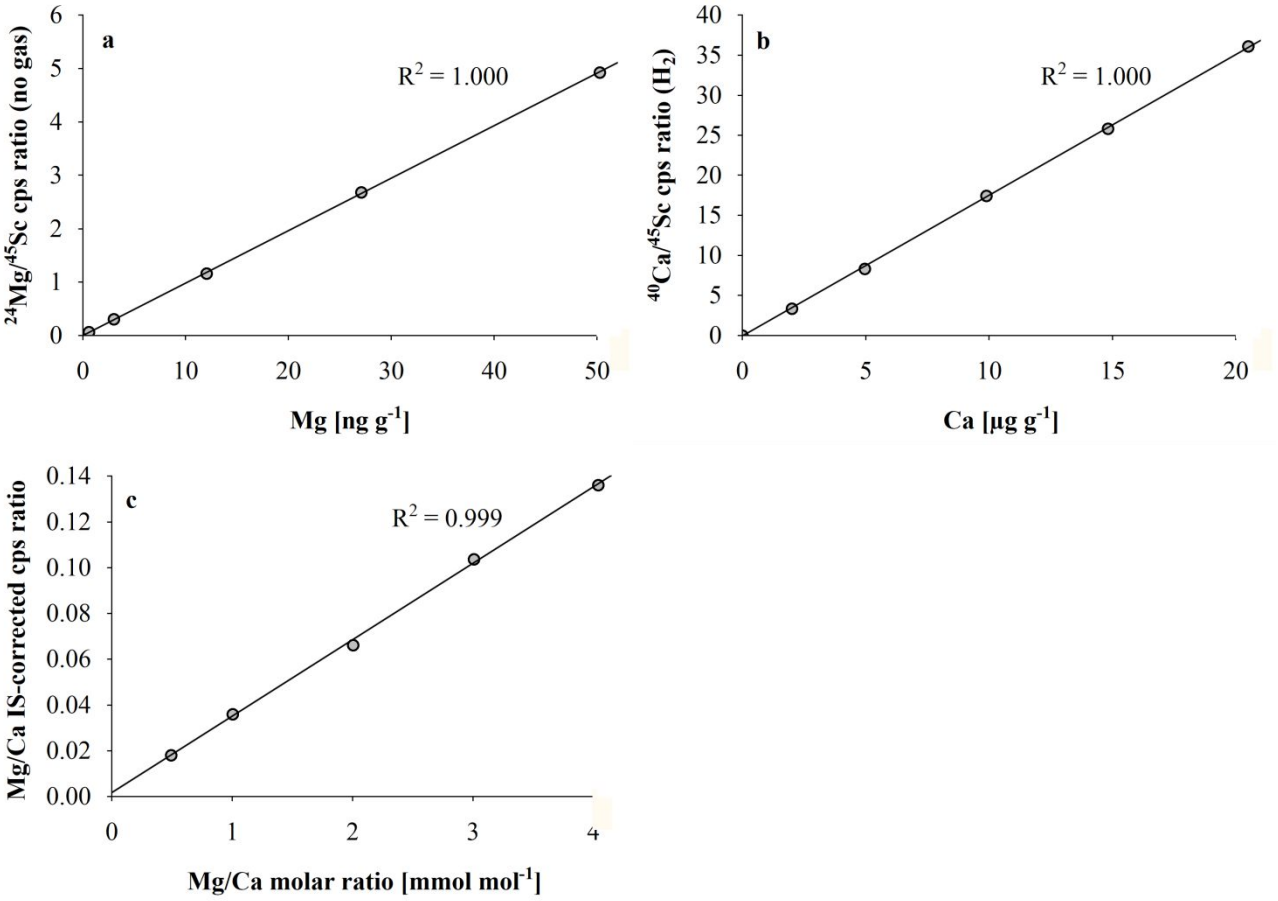

a
$R^2 = 1.000$
$^{24}Mg/^{45}Sc$ cps ratio (no gas)
Mg [ng g^{-1}]
b
$R^2 = 1.000$
$^{40}Ca/^{45}Sc$ cps ratio (H_2)
Ca [µg g^{-1}]
c
$R^2 = 0.999$
Mg/Ca IS-corrected cps ratio
Mg/Ca molar ratio [mmol mol^{-1}]

Fig. 3

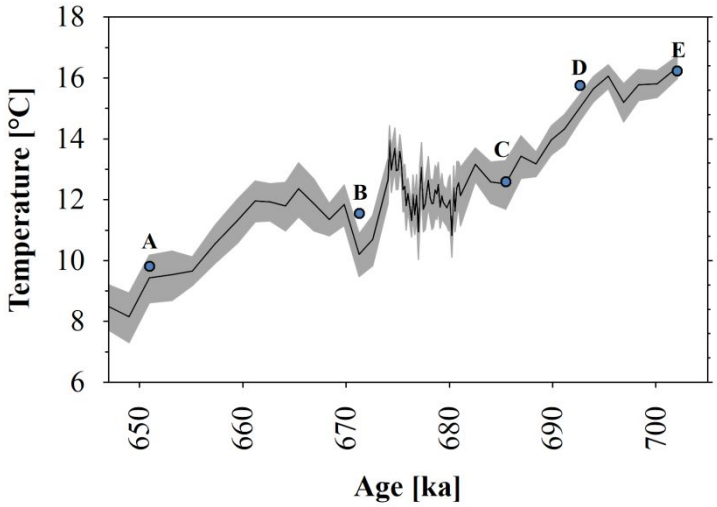
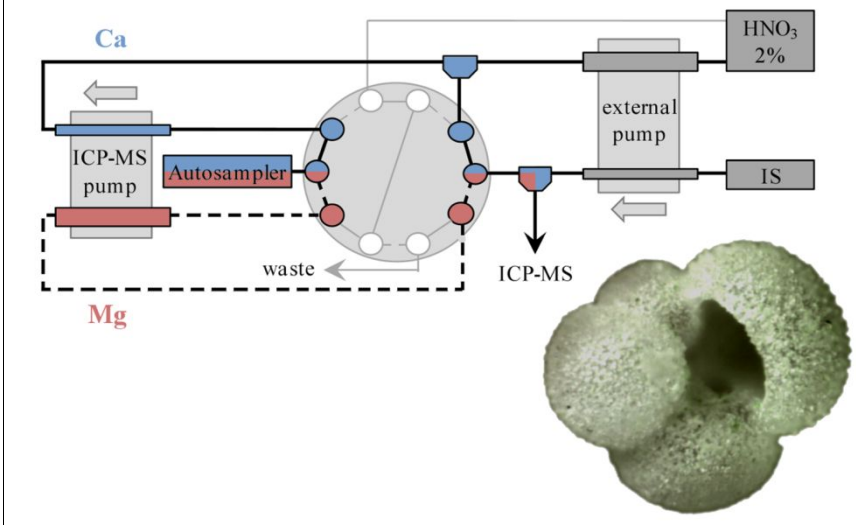
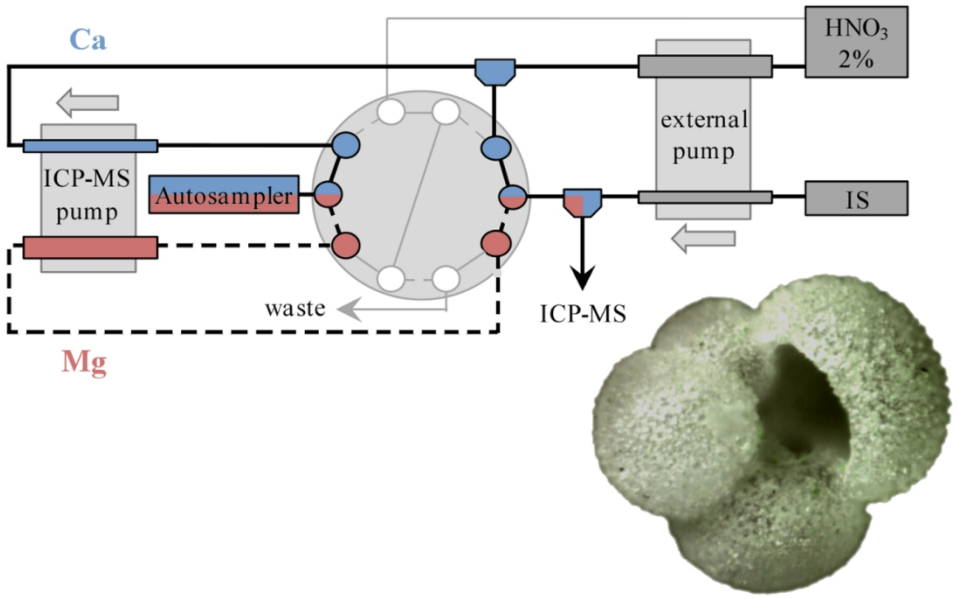

Temperature [°C]
18
16
14
12
10
8
6
650
660
670
680
690
700
Age [ka]
A
B
C
D
E

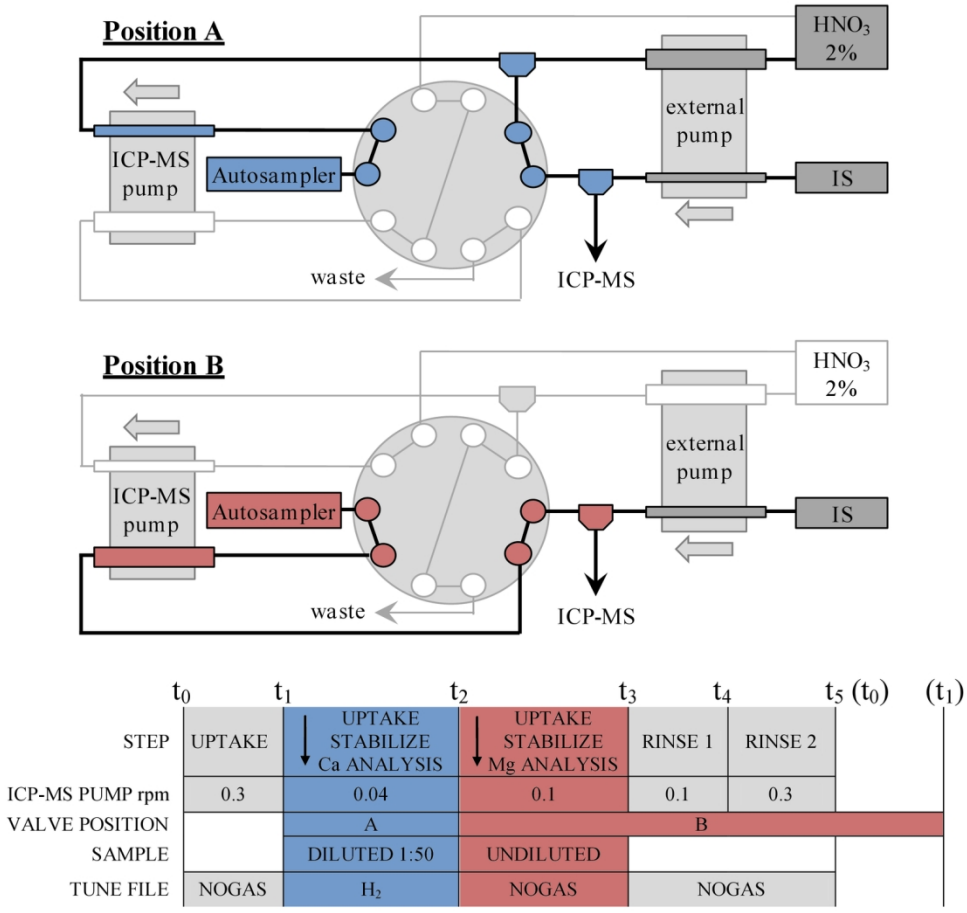
Fig. 4



Graphical abstract

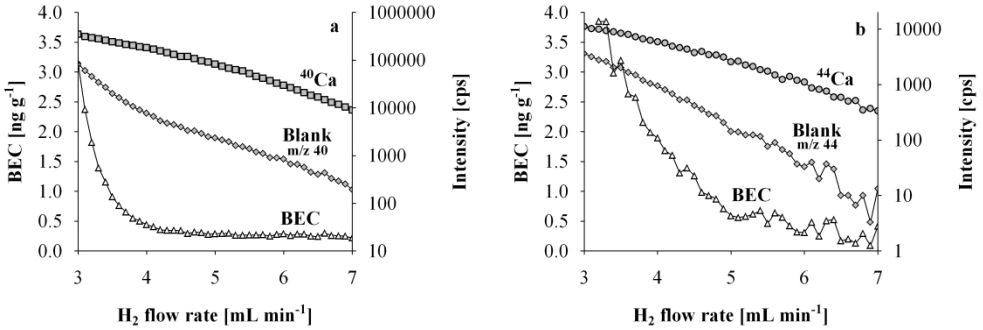


396x254mm (96 x 96 DPI)



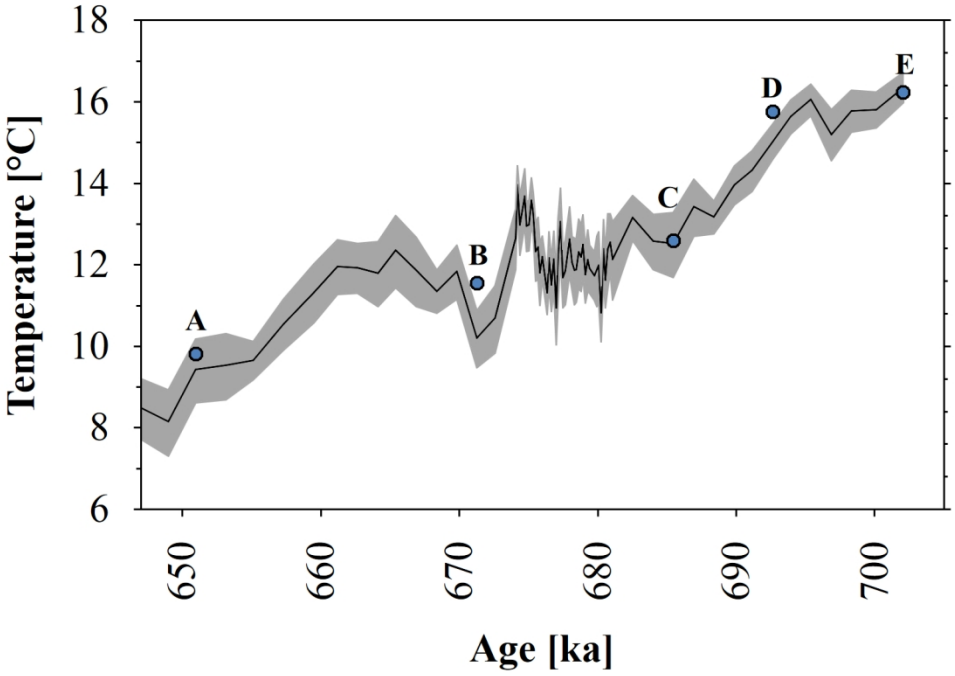
Above: scheme of the sample introduction set-up for the automatic on-line implementation of a dual dilution strategy. The two positions A and B of the 10-ports switching valve are represented. Tygon tubes were: two stops 1.65 and 0.25 mm i.d. for HNO3 and IS (respectively) for delivery by the external pump; three stops 1.02 and 0.25 mm i.d. for concentrated and diluted (respectively) sample delivery by the ICP pump. The bold lines mark the flow delivered to the ICP-MS. Below: scheme of the synchronised cyclic ICP-MS/valve time programme.

141x136mm (300 x 300 DPI)



Effect of H2 flow rate on the sensitivity and background equivalent concentration (BEC) for m/z 40 (a) and 44 (b) measured in a standard solution of Ca 100 ng g-1 and a blank solution.

899x312mm (96 x 96 DPI)



Shallow subsurface temperature estimates at Site U1313, based on Mg/Ca from the mixed-layer-dwelling planktonic foraminifera G. bulloides. The black line and the grey area represent the values reported by Naafs et al.32 and the corresponding confidence band (± 1·combined SD).

436x312mm (96 x 96 DPI)